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MACROMOLECULES FOR INHIBITION OF CORROSION AND WEAR

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INTRODUCTION

Currently there are no known chemical compounds which function as both antiwear and corrosion inhibiting agents. Our earlier study (1) established that there is a synergistic relationship between corrosion and wear. Enhancement of passivity or a build-up of corrosion resistant film on rubbing surfaces reduces wear significantly.

Molybdenum disulfide and graphite are by far the best and most widely used lubricating agents for elevated temperatures and loads that are available today. However, they possess no intrinsic properties which enable them to also function as corrosion inhibiting agents. In fact, in certain cases they are known to cause corrosion.

For example, in the hydrolysis of molybdenum disulfide, acidic components can be produced which readily attack metal and cause corrosion. Graphite is electrochemically very noble compared to most bearing materials used today. It is, therefore, well known for its ability to form galvanic cells with them whenever there is presence of moisture or any anionic media; causing corrosion of bearing metals. In the area of corrosion inhibition, chromates, sulfonates, nitrites and molybdates, among others, have been well documented to inhibit corrosion under a variety of conditions. However, they are not used as antiwear additives because they rapidly oxidize organic materials.

BACKGROUND

Generally most corrosion inhibitors are not custom made items. Classically, the development of the largest class of corrosion inhibiting substances was based on their molecular size which allows them to adsorb on the metal surface and suppress metal dissolution and reduction reactions. Now, it is accepted that the effectiveness of inhibitors is better predicted by the nature of chemical bonds than by the mere sizes of the molecule and their adsorption characteristics. Since porphyrins were discovered as a potential source for corrosion inhibitors (2-5), a considerable amount of interest has been generated in a family of such macrocyclic compounds (6,7). In addition to porphyrins, phthalocyanines also open up an excitingly new field in corrosion inhibition. Structurally, both of these parent compounds are similar with some subtle differences. The macrocyclics of these types are extremely stable, highly planar and possess high electron density in the pi-orbital system of the molecule for strong interactions with the conduction band of the surface metal atoms (8-13). Their generalized structures are as shown in Figure 1.

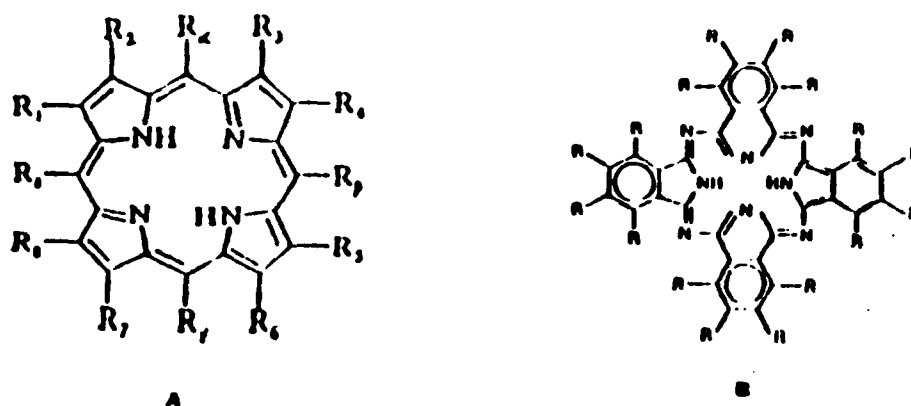


Figure 1 - Chemical structures of (A) porphyrins and (B) phthalocyanines.

Research on the lubricating properties of macrocyclic compounds and their corrosion inhibiting ability has uncovered another class of compounds (14) which possess the unique duality of antiwear and corrosion protection, simultaneously. These compounds are identified as Schiff bases which are the product of the chemical reaction between an aldehyde and an amine. In addition to their planar structure and quadridentate metal bonding characteristics similar to those of porphyrins and phthalocyanines, the Schiff base compounds exhibit appropriate thermal stabilities. Figures 2 and 3 show the reactions leading to some representative Schiff base chemical structures.

EXPERIMENTAL

POTENTIODYNAMIC POLARIZATION STUDIES

The effectiveness of phthalocyanines as acid corrosion inhibitors for steel was studied by conventional electrochemical dc and ac techniques. The details of these tests have been reported elsewhere in the literature(15-16). A rotating disk electrode at 1800 RPM (30 Hz) was been used for the polarization measurements.

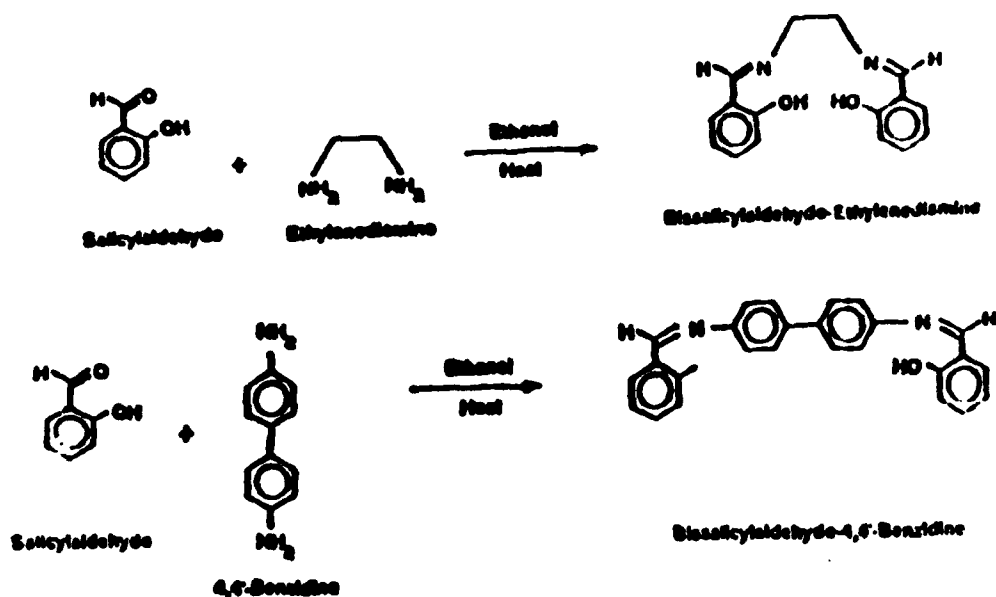


Figure 2 - Synthesis of various Schiff base Compounds.

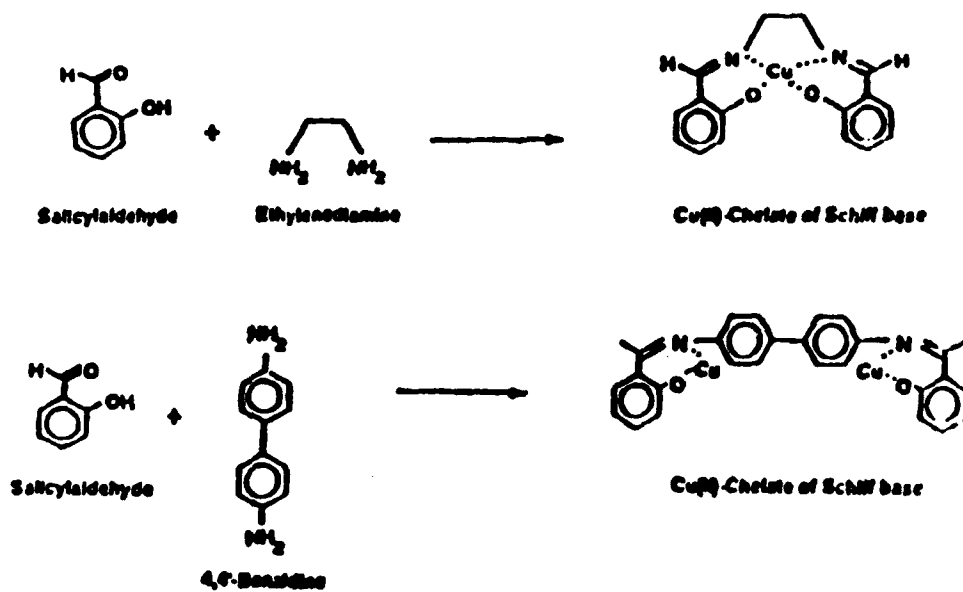


Figure 3 - Synthesis of various copper chelated Schiff base compounds.

To study polyphthalocyanine coatings for corrosion inhibition, the electrochemical testing was performed with a rotating cylinder electrode instead of using a rotating disk arrangement (17). This change was deemed necessary because it was not possible to heat treat the phthalocyanine coated metal disk at 450 C due to the inability of the Teflon mount to withstand such temperatures. The problem was overcome by using a removable cylinder electrode. Additionally, since the rotating cylinder electrode renders mass transfer rates much faster at reasonably slow rotational speeds, all the experiments with polyphthalocyanine coatings were performed with a rotating cylinder electrode at a rotational speed of 255 RPM.

AC-IMPEDANCE MEASUREMENTS

The ac-impedance studies on polymeric phthalocyanine coatings were studied at the free corrosion potential by holding the potential at this value, using a PAR Model 173 potentiostat. The impedance measurements over a wide frequency range (1 kHz to 10 MHz or less) were made with the help of a Solartron Model 1250 Transfer Function Analyzer. The amplitude of the ac signal used was 8 mV. Evaluation of the corrosion behavior of a polymer-coated metal, such as that used in this case, was made possible by the wideband ac impedance measurements, which provided information on both the resistive and the capacitive behavior of the interface.

INSTRUMENT BEARING TESTS

Instrument bearing tests were performed in accordance with ASTM Method D-3337, Standard Method for Evaluation of Greases in Small Bearings(18), under the test conditions given below.

TEST CONDITIONS USED FOR INSTRUMENT BEARING TESTS

Bearing Size: R-4 (6.35 mm bore dia.) stainless steel

Load: 2.2N radial, 22N axial

Speed: 12,000 rpm

Temperature: 204°C

Grease Wt.: 75mg

RESULTS AND DISCUSSION

CORROSION INHIBITION OF PHTHALOCYANINES

The study of phthalocyanines was directed to explore their ability to act as acid corrosion inhibitors for steel. It was believed that phthalocyanines would be more effective as corrosion inhibitors than porphyrins because of the almost rigid planarity of the phthalocyanine molecule. In addition to the chemisorption pathways, a higher degree of planarity is expected to increase the interaction between the pi-electron system of the phthalocyanine with the conduction band of the metal. Furthermore, the more planar the molecule, the higher degree of coverage and hence a higher inhibition efficiency. The planarity and electron density in the pi-system of molecules affect their surface adsorption properties and are specifically useful for the formation of stable films.

The study of polyphthalocyanines was considered more useful than their monomers in the respect that polyphthalocyanines could form a new revolutionary class of inhibitors because of their high electronic conductivity. An important feature here is that polyphthalocyanines while inhibiting corrosion are capable of retaining an important property expected from the metal, i.e. its electrical conductivity. This suggests some tremendously useful practical applications of electrically conducting coatings to protect sensitive electrical components from extraneous electromagnetic interferences.

Water soluble TSPC (see Table 1 for nomenclature) derivatives with metal centers were found to exhibit poor corrosion inhibition, as shown in Table 2. Water insoluble TAPC derivatives served as better corrosion inhibitors than their water soluble counterparts when the metal surface was coated with an adsorbed layer of the compound. The polarization plots (E vs. $\log i$) showed no significant differences in the presence or absence of phthalocyanines. A summarized view of the electrochemical parameters is reported in Table 2, indicating the influence of these monomers. Compared to Co(II)-TAPC, Fe(III)-TAPC showed higher degree of corrosion inhibition, however, the inhibitor efficiency was still far too low to be of any significance. Thus, the investigation centered on the formation of stable polymeric phthalocyanine coatings on the metal surface.

The results of the potentiodynamic polarization measurements for the mild steel in 1% NaCl solution (pH 2) with and without polymeric coatings were as shown in Figure 4. The number of distinct features noted from this figure are: (i) the corrosion potential shifted to more positive values with the polymer, Fe(III)-TCPC showed the most positive shift; (ii) both the anodic and cathodic polarization curves shifted to

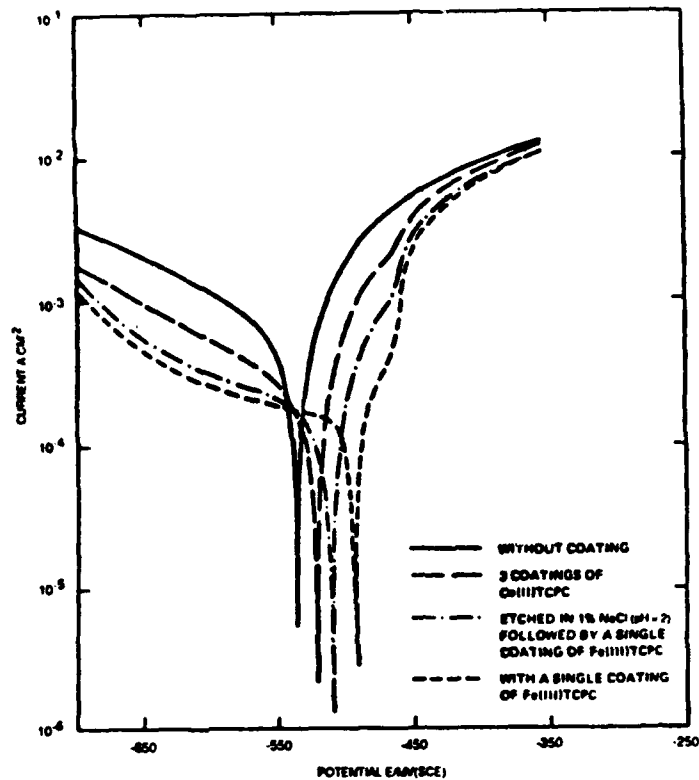


Figure 4 - The effects of phthalocyanines on the polarization behavior of mild steel in 1% NaCl solution of pH 2.

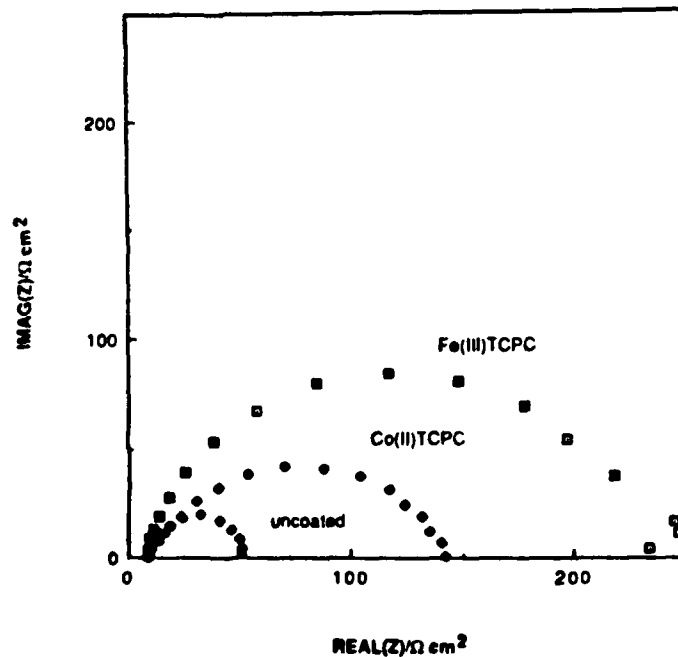


Figure 5 - Nyquist plots for mild steel in 1% NaCl solution (pH 2) with: (a) uncoated, (b) three coatings of Co(II)TCPC and (c) single coating of Fe(III) TCPC polymer.

Table 1

ABBREVIATIONS USED FOR VARIOUS PHTHALOCYANINE COMPOUNDS

<u>Designation</u>	<u>Nomenclature</u>
TSPC	tetrasulfo-phthalocyanine
TAPC	tetraamino-phthalocyanine
TCPC	tetracarboxy-phthalocyanine
TCAUPC	tetrakis-(N-carboxy-12-aminoundecanoic acid) phthalocyanine
TCACPC	tetrakis-(N-carboxy-6-aminocaproic acid) phthalocyanine

Table 2

RESULTS OF ELECTROCHEMICAL POLARIZATION MEASUREMENTS ON MILD STEEL TREATED WITH PHTHALOCYANINES IN 1% NaCl (pH 2).

<u>Inhibitor</u> <u>System</u>	<u>Ecorr</u> <u>mV(SCE)</u>	<u>mV/Decade</u>		<u>Icorr</u> <u>mA/cm²</u>	<u>% Inhibition</u> <u>Efficiency</u>
		<u>Ba</u>	<u>Bc</u>		
None	-500	45	-370	1.05	--
*VO-TSPC	-488	43	-350	1.0	5
*Co(II)-TSPC	-498	38	-300	0.95	10
*Fe(III)-TSPC	-490	39	-475	0.93	7
Co(II)-TAPC	-505	45	-325	0.95	10
Co(II)-TAPC	-493	43	-370	0.82	22
(on etched steel)					
Fe(III)-TAPC	-505	45	-340	0.65	37
Fe(III)-TAPC	-500	44	-372	0.88	16
(on etched steel)					

* 1 mM concentration in test solution (water soluble).

lower current densities; and (iii) the anodic reaction rates (polarization curves) were reduced by almost two orders of magnitude with the coatings. The results of these studies are summarized in Table 3.

Table 3

RESULTS OF ELECTROCHEMICAL POLARIZATION MEASUREMENTS ON MILD STEEL TREATED WITH POLYPHTHALOCYANINES IN 1% NaCl (pH 2).

Inhibitor System	E _{corr} mV(SCE)	mV/Decade		I _{corr} mA/cm ²	% Inhibition Efficiency
		B _a	B _c		
None	-538	247	-193	0.48	--
Co(II)-TCPC (3 coats)	-525	260	-205	0.20	55
Fe(III)-TCPC	-495	225	--	0.08	83
Fe(III)-TCPC (on etched steel)	-512	228	--	0.16	66

AC-impedance studies were also performed on the above polymeric coatings. The results of these experiments were shown as Nyquist plots [$\text{Re}|Z|$ vs. $\text{Imag.}|Z|$] of the interfacial impedance as a function of frequency, as in Figure 5. The curves, slightly suppressed semicircles, show the characteristics of steel in chloride solutions with and without the presence of polyphthalocyanines. The polarization resistance (R_p) values, calculated from these impedance spectra, were determined from the intercepts (lengths of the diameters) of the suppressed semicircles along the [$\text{Re}(Z)$] axis. As shown in Table 3, the R_p values increased 3 and 6 folds when three coatings of polymeric Co(II)-TCPC and a single coat of Fe(III)-TCPC were applied on the steel surface, respectively; the corresponding calculated inhibitor efficiencies were approximately 68% and 83%, respectively. Pre-treatment of the metal surface, such as etching, did not improve the bonding of the polymer Fe(III)-TCPC.

CORROSION AND WEAR INHIBITION OF MACROCYCLIC COMPOUNDS

Electrochemical polarization curves were generated for various Schiff base compounds, as shown in Figure 6. It can be observed that <0.001 molar unchelated Schiff base in 1% sodium chloride solution will protect a 1010 steel by decreasing anodic and cathodic currents by at least three orders of magnitude. This is interpreted as lowering the corrosion rates by the same order of magnitude. In contrast, the copper chelated Schiff bases were found to be ineffective in lowering corrosion currents. This suggested that the key to providing corrosion

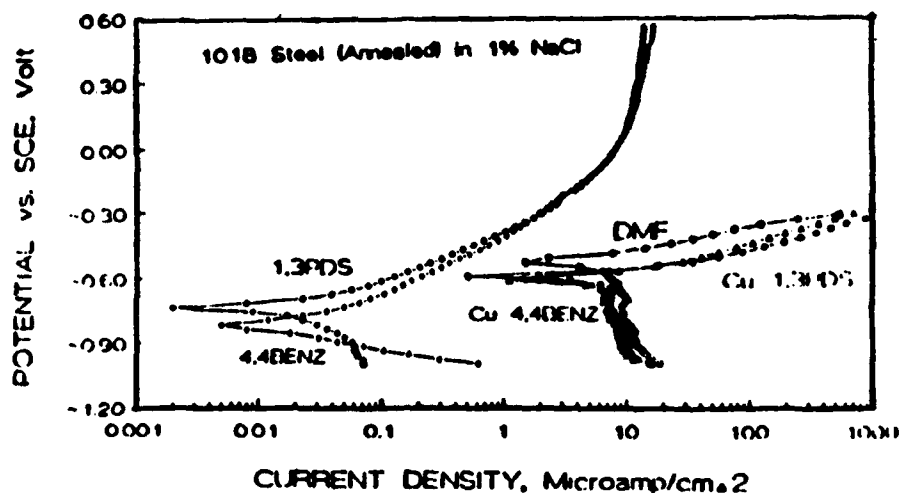


Figure 6 - Polarization curves for chelated and non-chelated Schiff bases [10^{-3} M] dissolved in 10 ml of DMF and dispersed in 1% NaCl (aqueous).

Table 4

RESULTS OF THE AC IMPEDANCE MEASUREMENTS ON MILD STEEL TREATED WITH MONOMER AND POLYMER PHTHALOCYANINES IN 1% NaCl SOLUTION (pH 2),

Inhibitor System	Rp in Ohm.cm ²	Wmax, rad./s	Cp in uF/cm ²	% Inhibition Efficiency
None	42	63	378	--
Poly Co(II)-TCPC (3 coats)	137	10	750	68
Poly Fe(III)-TCPC	240	13	318	83
Poly Fe(III)-TCPC (on etched steel)	159	16	400	74
Poly Fe(III)-TCPC ** (low void fraction)	174	2	3640	77
*Fe(III)-TCAUPC	323	16	196	88
*Co(II)-TCAUPC	243	4	1038	83
*Fe(III)-TCACPC	255	25	157	84
*Co(II)-TCACPC	114	40	222	65

- * Phthalocyanine containing long chain hydrocarbon groups: [TCAUPC] - tetrakis (N-carboxy-12-aminoundecanoic acid); [TCACPC] - tetrakis(N-carboxy-6-aminocaproic acid).
- ** Containing p-hydroxy pyridine groups in the voids.

protection involved the nitrogen centers on the Schiff base compounds. These sites reacted with the metal surface to provide corrosion protection.

The next phase of this study centered on investigating the effect of macrocyclic additives on the enhancement of lubricating properties of a high temperature grease. A perfluoropolyalkylether (PFPE) grease was chosen as the base line for comparison purposes since it is representative of the state-of-the-art for high temperature greases and any increase in wear life realized would extend functionality. The chemical structure of various PFPE fluids is shown in Figure 7. Structure (II) is representative of the type of fluid used in the current investigation.

The advantageous properties of PFPE fluids include: chemical resistance to hot hydrofluoric acid, liquid oxygen and strong bases as well as low vapor pressure and possessing a wide temperature range (-35°-300°C). Their "Achilles Heel" is caused by catalytic attack with Lewis Acids. As shown in Figure 8, in the presence of a typical Lewis Acid such as FeF_3 , the thermal stability of the fluid is reduced by about 30°C. On a kinetic scale, this can be interpreted as representing an eight fold decrease in stability.

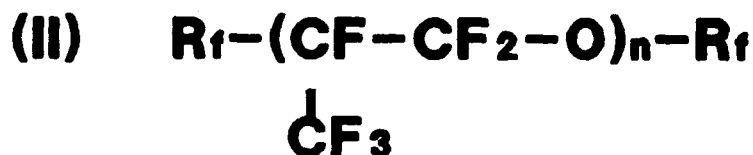


Figure 7: The chemical structure of various perfluoroalkyl-poluether (PFPE) fluids.

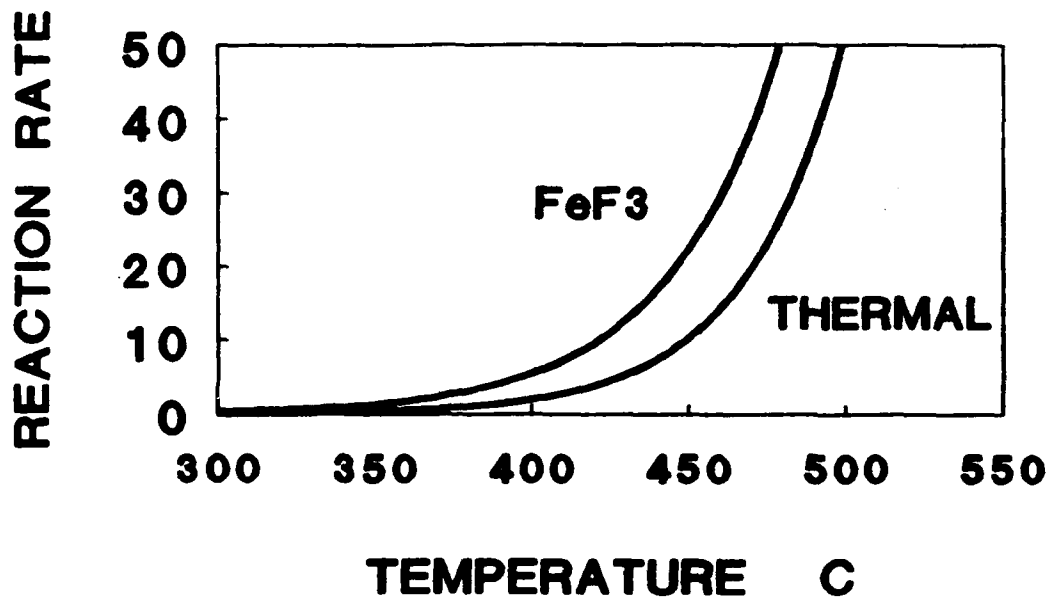
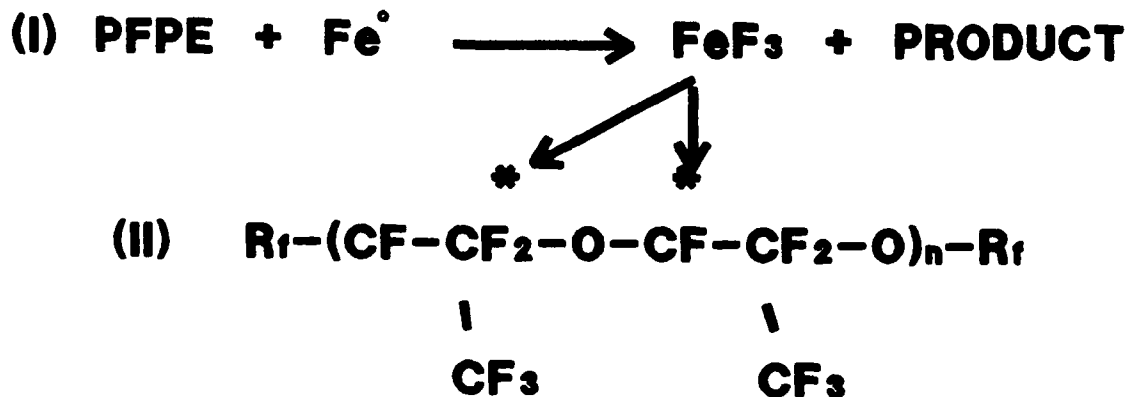


Figure 8: PFPE degradation in the presence of FeF_3 Lewis acid.



$\ast = \text{SITE OF REACTIVITY}$

Figure 9: The degradation mechanism of PFPE fluids operating in a steel bearing.

The implication of this phenomena for reducing lubricant life for bearings is shown in Figure 9. As the steel bearing wears, elemental Fe is produced which can react with the PFPE by extracting fluorine atoms and forming FeF_3 . The FeF_3 is then capable of catalyzing the degradation of PFPE by splitting its molecular structure at the sites indicated in Figure 9.

One approach that demonstrates the effect of altering this reaction scheme is to prevent exposure of the PFPE lubricant to Fe wear debris by coating the bearings with a ceramic such as TiN. As shown in Table 5, the wear life of TiN ceramic coated bearing is increased by a factor of 8.8, compared to the non-coated bearing.

Table 5

CERAMIC SURFACE EFFECT ON WEAR LIFE

BEARING MATERIAL	COATING	WEAR LIFE (hrs)	IMPROVEMENT FACTOR
440C	None	3.8	---
440C	TiN	33.3	8.8

TEST CONDITIONS:

* SPEED: 1750rpm	* LUBRICANT: PFPE OIL
* LOAD: 200N	* QUANTITY: 10uL
* TEMP: AMBIENT	

Table 6

THE MELTING POINT AND THERMAL STABILITY OF SELECTED SCHIFF BASE COMPOUNDS

SCHIFF BASE	MP ($^{\circ}\text{C}$)	%WT. LOSS AT 350 $^{\circ}\text{C}$	
		AIR	NITROGEN
Ethylenediamine Salicylaldehyde	123	70	58
1,3-Phenylenediamine Salicylaldehyde	105	37	24
4,4'-Benzidine Salicylaldehyde	264	3	0

A less expensive approach toward achieving the same results involved the use of Schiff base compound as an additive to the PFPE grease. Table 6 shows the melting point and stability properties of selected Schiff base compounds. The 4,4' benzidine-salicylaldehyde Schiff base was observed to possess one of the highest melting points and in addition was the most stable in air and nitrogen at temperatures as high as 350°C. Figure 10 and 11 show the DSC thermograms obtained on for the 4,4' benzidine-salicylaldehyde Schiff base in nitrogen and air, respectively.

Table 7 shows the results of Instrument Bearing tests conducted on various grease formulations containing macrocyclic compounds of phthalocyanine and Schiff base types incorporated into the grease at a concentration of 5 w/o. The most striking improvement in wear life was observed with a Schiff base of 4,4' Benzidine and Salicylaldehyde, which exhibited an improvement ratio of 16.4 in comparison to the uninhibited grease. Phthalocyanine and other Schiff bases exhibited only slight improvement ratios ranging from 1.2 to 1.8. The copper chelate of 4,4' Benzidine and Salicylaldehyde showed no improvement.

Table 7

R-4 INSTRUMENT BEARING TEST RESULTS
(PERFLUOROLPOLYALKYLETHET GREASE)

Additive (5w/o)	Avg. Wear Life, hrs	Improvement Ratio
1. None	65	--
2. Phthalocyanine	78	1.2
3. Schiff base of 4,4' Benzidine & Salicylaldehyde	1067	16.4
4. Cu chelate of #3	41	0.6
5. Schiff base of 1,3 Phenelynediamine & Salicylaldehyde	104	1.6
6. Cu chelate of #5	110	1.8

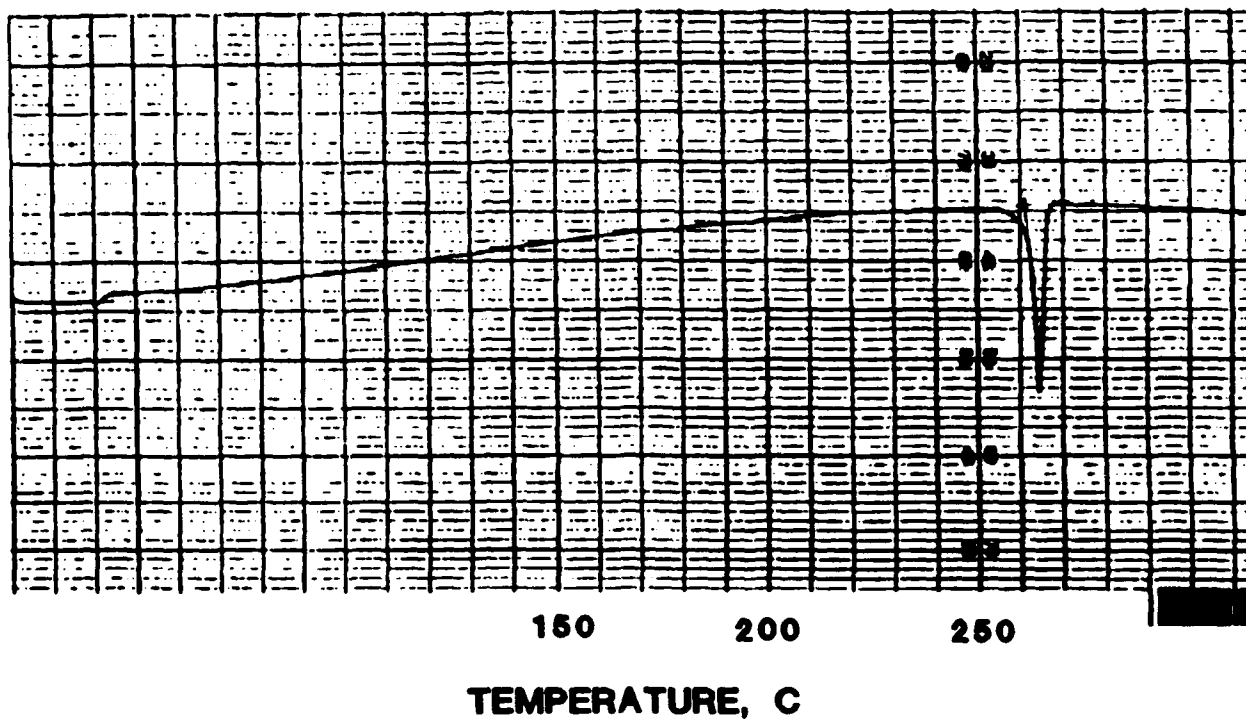


Figure 10: DSC thermogram of 4,4'-benzidine-salicylaldehyde in nitrogen.

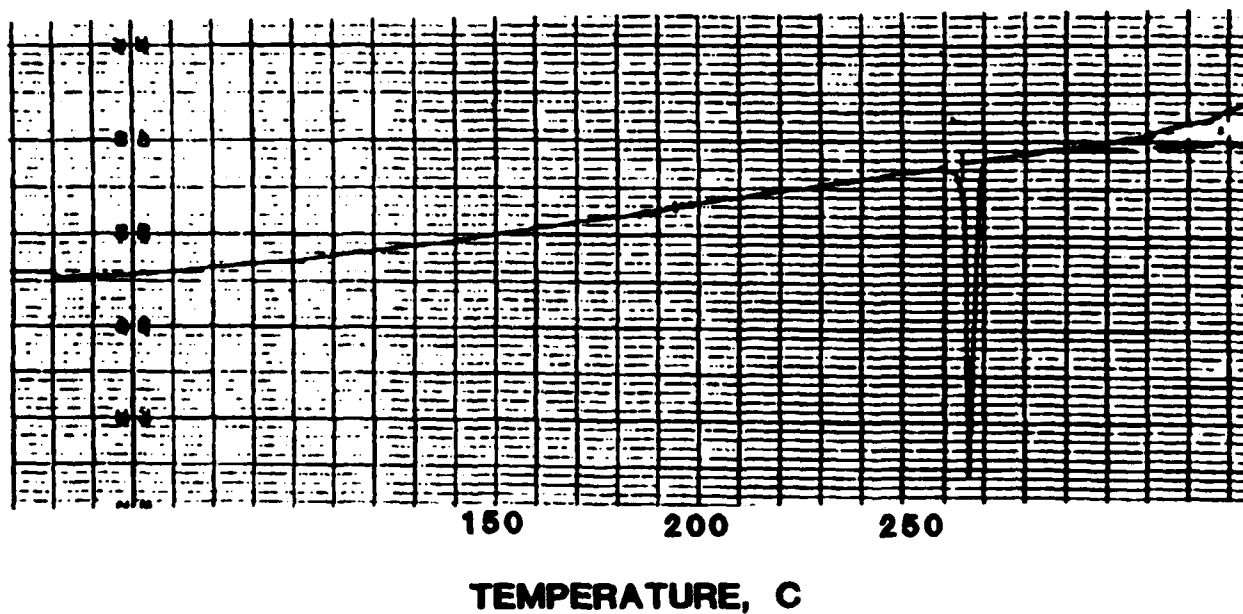


Figure 11: DSC thermogram of 4,4'-benzidine-salicylaldehyde in air.

From previous studies (19) it was determined that the key to achieving extended lubricant life with PFPE high temperature lubricants is to prevent their degradation as a result of Lewis-Acid catalysis. Although PFPE lubricants are considered to be one of the most stable lubricating media, their one weakness is their reactivity with metals, such as Fe, which are generated during the wear process. Fe reacts with C-F to form $\text{FeF}_2/\text{FeF}_3$ (Lewis-Acids) which further catalyzes degradation. The action of Schiff base additives is essentially to minimize or eliminate this degradation process by "chelating" with Fe (either on the surface or as wear debris) at their nitrogen centers. Also reactivity at the bearing surface was found to play a key role in achieving extend life. This same reactivity is responsible for their corrosion protection capability. This duality (antiwear and corrosion inhibition) is unique to Schiff base additives. That reactivity at the nitrogen centers plays a key role is demonstrated by the fact that synthesized "chelated" Schiff Bases exhibited only limited to no improvement in wear life ratios and no improvement in corrosion protection.

CONCLUSION

In general, macromolecules have shown good corrosion inhibition properties and, seemingly due to their high configurational electron density and bonding characteristics, i.e. reactivity of the nitrogen centers with the metal surface. It was also concluded that a similar mechanism applies to develop wear resistance, compounds which were chelated had shared nitrogen atom activity, and thus, showed poorer resistance to wear and corrosion. However, for a compound to exhibit duality (both wear and corrosion inhibition) in a formulation such as grease, it was necessary for the medium (grease) to provide activation energy for bonding with the metal surface. It was determined that fluorides in the grease were a combining factor. This was shown for Schiff bases when formulated in fluoride containing lubricants. In particular, Schiff base of 4,4' benzidine and salicylaldehyde in PFPE (perfluoropolyalkylether) showed a 16 fold improvement in bearing life of the R-4 bearing, whereas non-fluorinated lubricants showed no significant improvement. Here, the tribochemical actions in the presence of fluoride were able to create bonding with the Schiff base compound to form a passive film of the metal.

Application of Schiff base inhibitors to lubricant formulations will increase the "Mean Time Before Failure" (MTBF) of bearings, splines, gears and rotors by several orders of magnitude over current state-of-the-art materials. In addition, temperature excursions of 50C can be tolerated without undue concern for reduction in life expectancy. Bearing assembly failures due solely to corrosion will be greatly diminished or completely eliminated. As a result of these aforementioned benefits, reduced maintenance man-hours will be realized especially for instrument bearings which are often located in difficult to access areas and require costly maintenance procedures.

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